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EXPLORING IN AEROSPACE ROCKETRY

4. THERMODYNAMICS

by Marshall C. Burrows  
Lewis Research Center  
Cleveland, Ohio

Presented to Lewis Aerospace Explorers  
Cleveland, Ohio  
1966-67



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**Advisor, James F. Connors**

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## 4. THERMODYNAMICS

Marshall C. Burrows\*

By using the equations which were presented in chapter 2, it can be shown that specific impulse, or the pounds of force exerted by the rocket per pound of propellant flowing each second, is dependent on the composition and temperature of the combustion products. Therefore, studying the various kinds of propellants and noting what happens when they react or burn is important. Observing how fast heat is produced by each pound of propellant that enters the combustion chamber is also important, since this determines the size and weight of the chamber.

The study of propellants, their reactions, and the energy changes needed to perform work is called thermodynamics. This practical subject gives engineers many tools they need to improve systems that interchange energy and work. Some such systems are rocket engines, automotive engines, and even refrigerators. We will not concern ourselves with the details of this subject but will only examine several rules or laws of thermodynamics that are important to remember. The first rule concerns temperature, a term which we hear applied to the weather every day. The point to remember is that a group of bodies (or molecules) all at the same temperature are said to be in "thermal equilibrium" with each other. The second rule to remember is that we cannot get more useful energy out of a system than we put into it. In other words, we cannot get more useful thrust out of a rocket engine than we put into it in the form of energy-containing propellants. This is analogous to the adage which states that "you can't get something for nothing." The final rule that we will consider is that heat flows only from hotter to cooler bodies. Many novel methods of propelling a rocket engine have failed because the inventor forgot one of these basic rules. Even the refrigerator in your home obeys these rules. The fluid that absorbs heat from the inside of the box is compressed and pumped to the bottom or back of the refrigerator where heat is rejected to the room.

Now that we have discussed some rules which govern the operation of a rocket engine, we shall examine in greater detail the characteristics and combustion processes of some available propellants.

The first genuine rocket propellant was probably made by the Chinese for their "arrows of flying fire" in the 13th century. Ingredients may have included tow, pitch,

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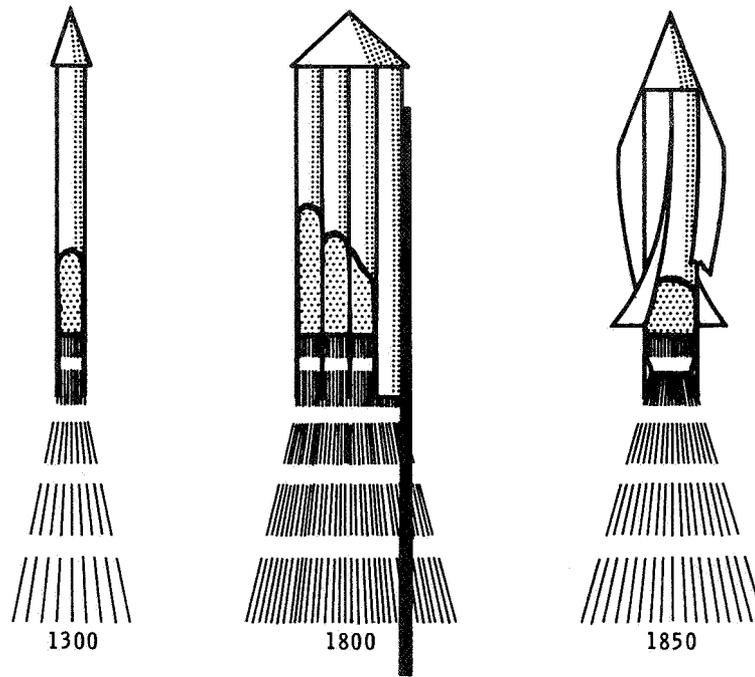


Figure 4-1. - Early solid-propellant rockets.

turpentine, sulfur, charcoal, naphtha, petroleum, incense, and saltpeter. Eventually, gunpowder (or black powder) became the standard propellant, first in powder form, and later in granular form. In all the early solid-propellant rockets, burning proceeded upstream from the nozzle in a rather uncontrolled manner. Figure 4-1 shows how these early rocket configurations progressed from simple "fire arrows" to spin-stabilized missiles. Late in the 19th century it was found that combustion could be controlled more reliably if the powder was pressed into pellets or "grains." This latter term is still used today to define a propellant charge.

Near the end of the 19th century, a double-base (nitrocellulose-nitroglycerine) propellant was introduced, and it partly replaced the traditional gunpowder. The smokeless exhaust of this new propellant was a significant advantage for military uses.

The first use of liquid propellants in rockets was claimed by Pedro E. Paulet, in Peru in 1895, when he operated a small rocket on gasoline and nitrogen peroxide. Robert H. Goddard, an American, demonstrated a gasoline - liquid-oxygen rocket in 1926, and he has been considered the pioneer in this field. Work on the improvement of the liquid-propellant rocket continued throughout the 1930's. This work enabled the Germans to build a workable missile in the form of the V-2 rocket during World War II. The variation among these early liquid-propellant rockets is shown in figure 4-2.

Work on both liquid and solid propellants has been accelerated since that time until we now have a variety of liquids and solids from which to choose. The most common liquid propellants are listed in table 4-I. Liquid oxygen and alcohol powered the V-2

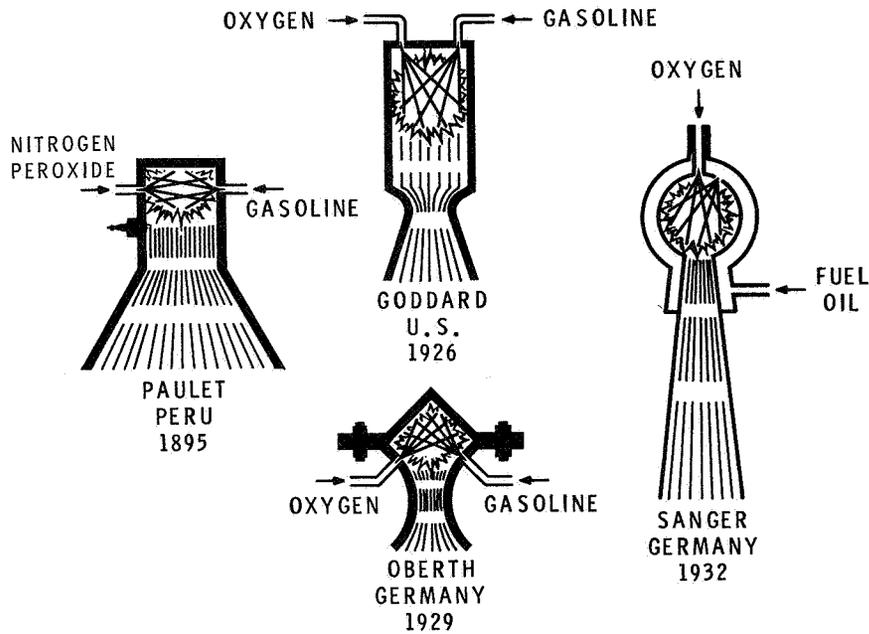
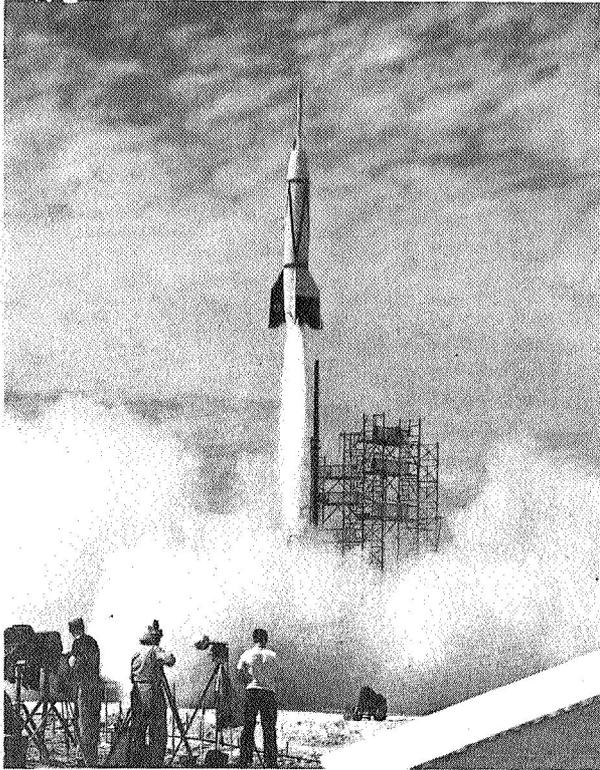


Figure 4-2. - Early liquid-propellant rockets.

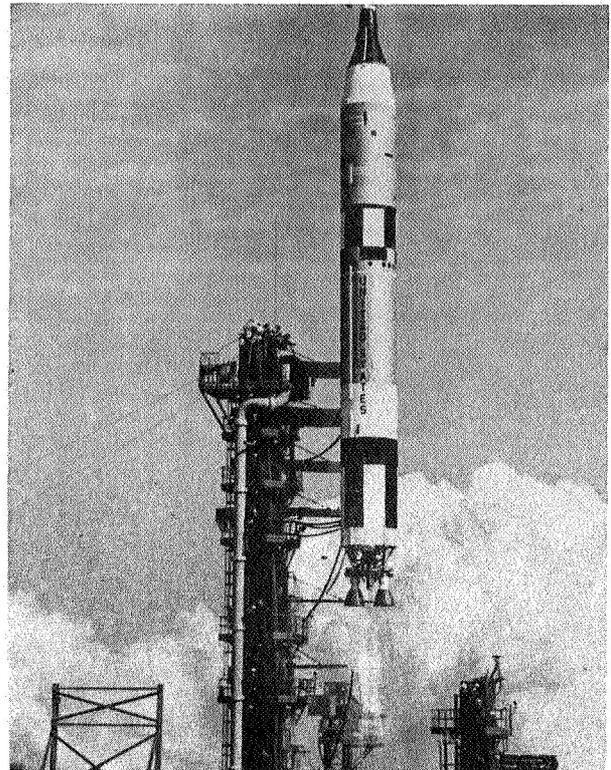
TABLE 4-I. - COMMON CHEMICAL-ROCKET-PROPELLANT COMBINATIONS

Oxidizer			Fuel			Typical oxidant-fuel weight ratio, O/F	Specific impulse, (lb)(sec) lb (a)
Name	Formula	Storage temperature, °F	Name	Formula	Storage temperature, °F		
Liquid							
Oxygen	O <sub>2</sub>	-297	Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH	60	2.00	287
Nitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	60	Hydrazine	N <sub>2</sub> H <sub>4</sub>	60	1.30	291
Oxygen	O <sub>2</sub>	-297	RP-1 (kerosene)	-----	60	2.60	301
Oxygen	O <sub>2</sub>	-297	Hydrogen	H <sub>2</sub>	-423	4.00	391
Solid							
Potassium perchlorate	K <sub>4</sub> ClO <sub>4</sub>	60	Asphalt resin	(CH <sub>2</sub> ) <sub>x</sub>	60	High	220
Ammonium perchlorate	NH <sub>4</sub> ClO <sub>4</sub>	60	Rubber or plastic resin	-----	---	High	250
Double-base type propellant (nitrocellulose-nitroglycerine); boiling point, 60° F						----	250

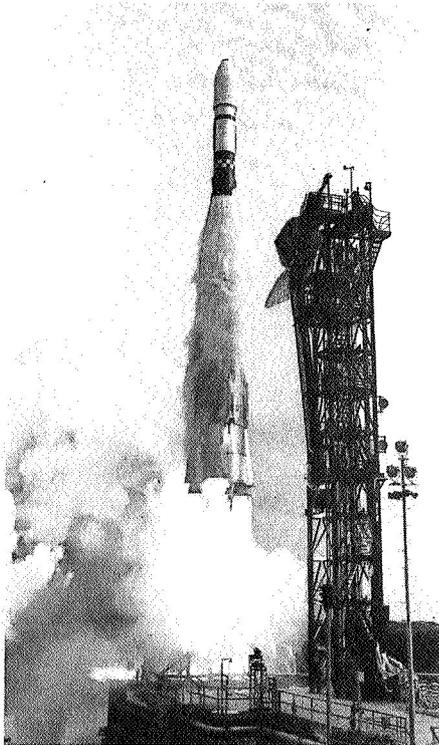
<sup>a</sup>Maximum theoretical impulse for products expanding from a combustion-chamber pressure of 1000 lb/in.<sup>2</sup> to atmospheric pressure.



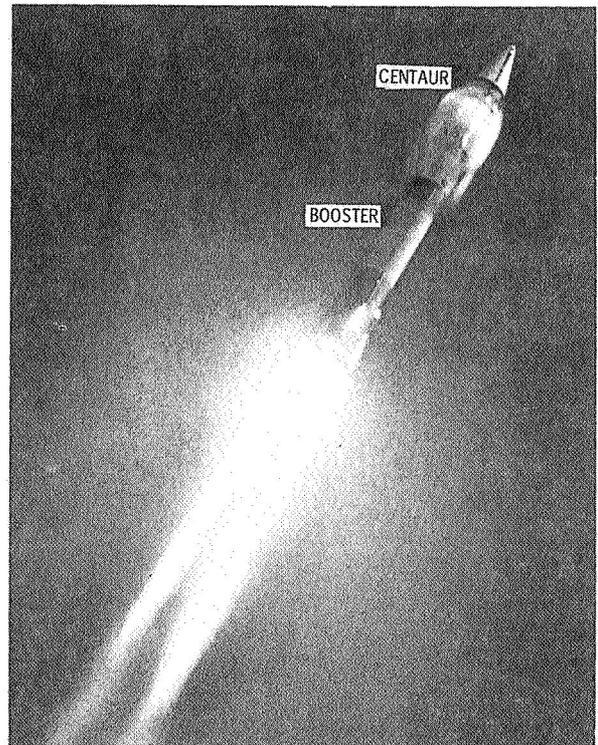
(a) Modified V-2 booster. Propellant, liquid-oxygen - ethyl alcohol.



(b) Titan II booster. Propellant, nitrogen tetroxide - Aerozine.



(c) Atlas booster. Propellant, liquid oxygen - RP-1.



(d) Centaur upper stage. Propellant, liquid oxygen - liquid hydrogen.

Figure 4-3. - Liquid-propellant applications.

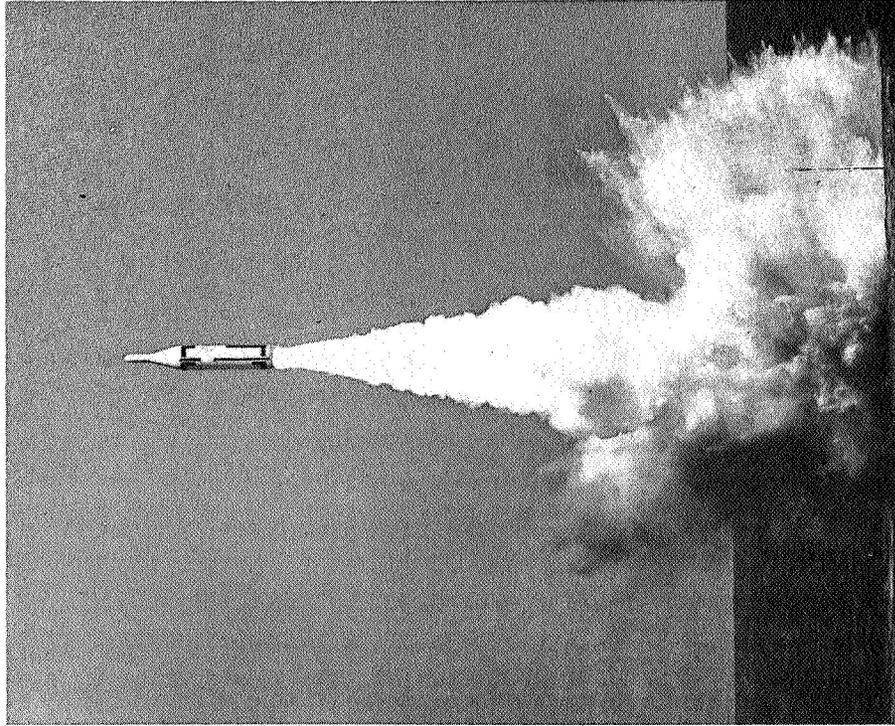
rocket (fig. 4-3(a)) that we mentioned earlier. Oxygen is liquid only at very low temperatures, so it must be refrigerated or stored in well-insulated tanks. From the standpoint of storage, the second set of propellants is attractive. Nitrogen tetroxide is the oxidizer, and hydrazine is the fuel. Both of these propellants are liquid in the temperature range of 40<sup>o</sup> to 70<sup>o</sup> F. Both propellants are very toxic, and hydrazine can burn alone, or act as a "monopropellant." This property of hydrazine can cause it to be dangerous to handle or use when it is heated excessively. However, when hydrazine is mixed with an equal amount of another liquid fuel called UDMH (unsymmetrical dimethyl hydrazine), the resulting mixture (Aerozine) is reasonably safe to use. Nitrogen tetroxide and Aerozine were used in the Titan II boosters (fig. 4-3(b)) which launched the Gemini series of manned satellites. Liquid oxygen has been used with RP-1 and hydrogen to power several important rocket vehicles. RP-1 is a type of kerosene, and, with liquid oxygen, powers the Atlas booster (fig. 4-3(c)). Hydrogen is liquid at a much lower temperature than oxygen. It is much more energetic than the other fuels, but it is very light as a liquid, just as it is very light as a gas. Hence the tank that holds the hydrogen must be large in volume and very well insulated. The Centaur (fig. 4-3(d)), which operates in a space environment, uses liquid hydrogen and liquid oxygen as propellants.

Other oxidizers that are used in liquid propellant systems are fluorine, fluorine compounds, nitric acid, and hydrogen peroxide. Other liquid fuels include ammonia, metallic hydrides, various hydrocarbons, and amines.

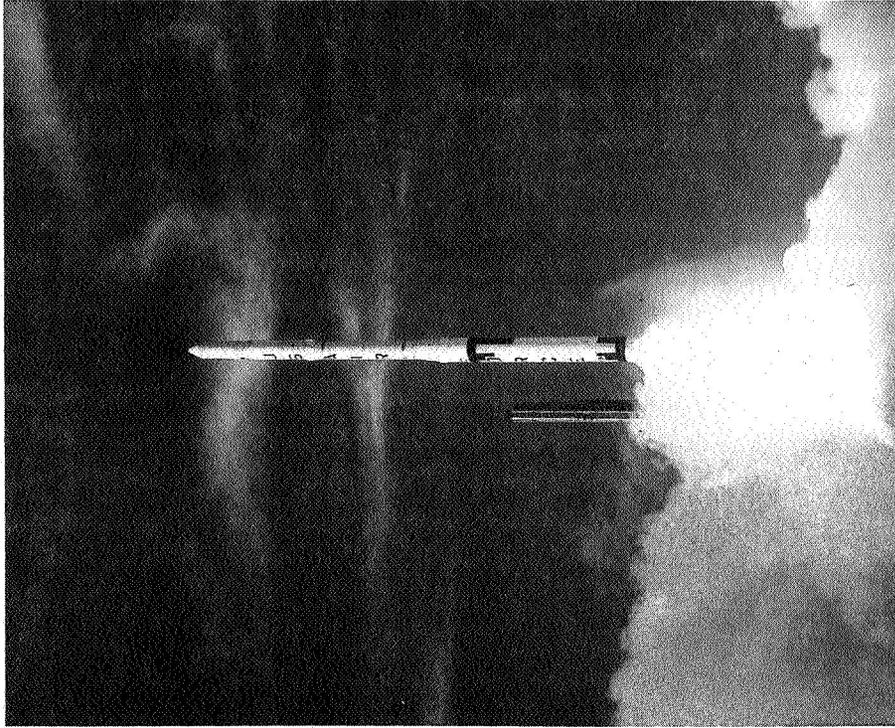
Despite the poor performance and bad physical properties of gunpowder, it is still used as a solid propellant. For example, Model Missiles, Inc., uses sporting black powder in its Type A motors for missile model propulsion. However, new composite propellants are replacing it because their performance is much higher, and their physical properties are much improved.

In table 4-I the most common solid propellants are listed. The first new composite that resulted from research work early in World War II consisted of a mixture of potassium perchlorate oxidizer and asphalt resin fuel. This combination was used in the initial JATO (Jet Assisted Take-Off) units. Ammonium perchlorate was soon substituted as the oxidizer, and plastics or synthetic rubbers replaced asphalt resins as the fuel. These combinations yielded considerably less smoke in the exhaust, produced higher impulse, and presented fewer handling problems than previous composite propellants. The Polaris and Blue Scout boosters (fig. 4-4) use improved types of composite propellants.

The double-base propellant has been used for various military rocket applications since Robert Goddard first experimented with it during World War I. The three major materials used are nitrocellulose, nitroglycerin, and diethylene glycol dinitrate (DEGN). Unfortunately, each of these materials is about as hazardous as the mixed composite pro-



(a) Polaris missile. Composite propellant grain.



(b) Blue Scout booster, composite propellant grain; third stage, double-base propellant grain.

Figure 4-4. - Solid-propellant applications.

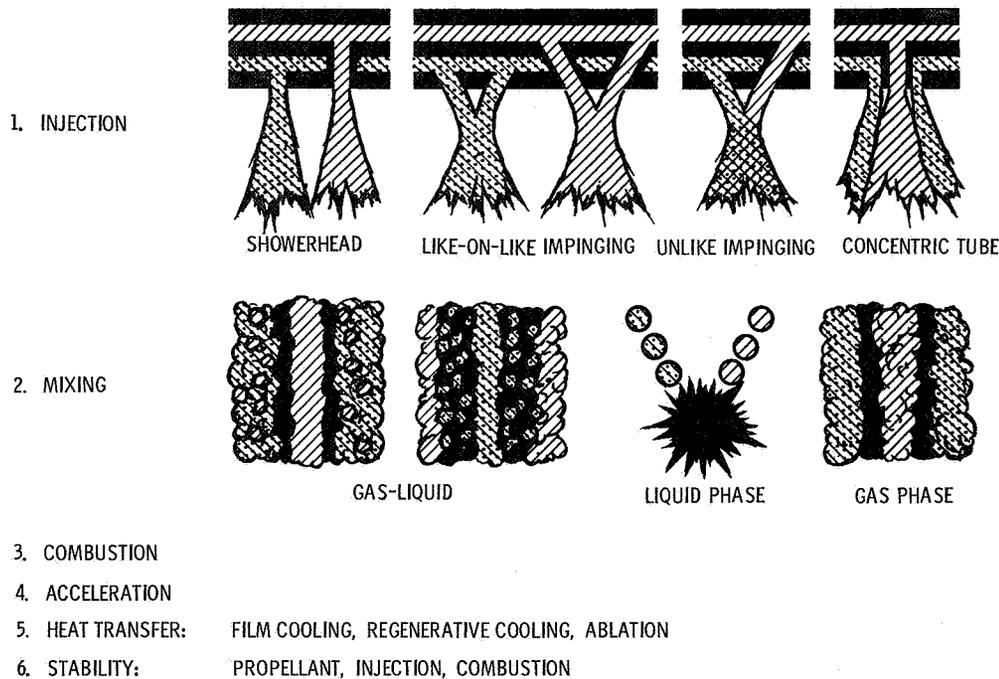


Figure 4-5. - Liquid-propellant combustion.

pellant. Dry nitrocellulose, nitroglycerin, and DEGN are all high explosives and sensitive to shock. Mixing and forming are always done remotely, and numerous materials are added to increase the safety and reliability of the propellant. The Nike booster and the final stage of the Blue Scout utilize homogeneous propellants.

Now that the common types of propellants have been described, let us consider the manner in which the two basic types of propellant, liquid and solid, burn to produce hot, gaseous products.

Figure 4-5 shows various means of injecting liquid propellants into the combustion chamber. These means of injection include showerhead jets, impinging streams of several types, and concentric tubes in various sizes and arrangements. Injection of the propellant is followed by the mixing process. There are four processes by which liquid propellants may mix. Cold liquids such as oxygen and hydrogen may be near their boiling temperatures when they enter the combustion chamber. On the other hand, liquids such as RP-1 (kerosene) must be heated up to their boiling temperatures by the combustion gases themselves. Hence, one mixing process is that of slowly heating fuel droplets and streams surrounded by vaporized oxidizer. Oxygen-alcohol and oxygen - RP-1 propellants mix by this process because the oxygen vaporizes before the alcohol or the RP-1. In a second mixing process oxidizer droplets are surrounded by vaporized fuel. Oxygen-hydrogen propellants mix by this process because the vaporization of hydrogen exceeds that of the oxygen. Liquids that react spontaneously (hypergolic pro-

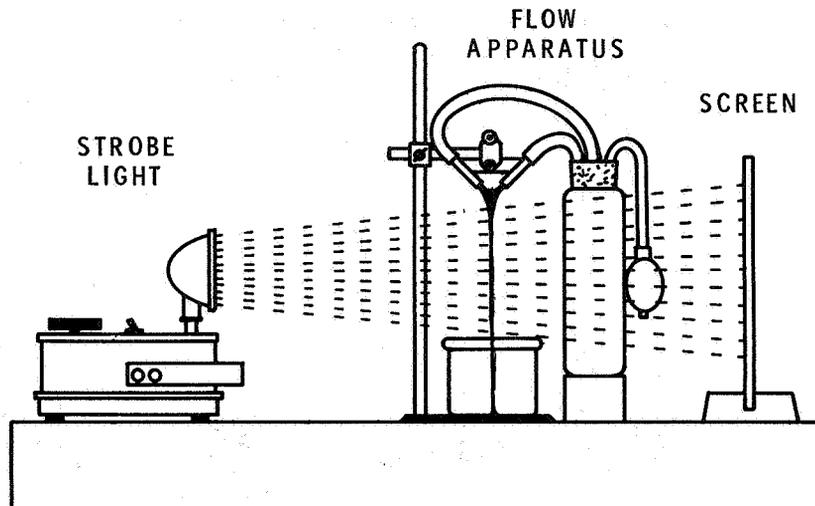


Figure 4-6. - Cold-flow injection apparatus.

pellants) mix by a third process. In this process, neither of the ingredients is boiling, but they mix as liquids. The liquids then react at their interfaces or from within to break up the liquid streams into droplets and vaporized gases. A fourth process is the mixing of gases. This process occurs in gaseous-propellant rockets or where liquids have been heated so that they enter the combustion chamber as gases.

The injection and mixing processes can be observed in cold flow tests with an apparatus like that shown in figure 4-6. When water or one ingredient of the propellant mixture is flowed through the injector, the spray pattern shows the extent of propellant mixing and the size of the droplets produced in the mixing process. The injection behavior of nonboiling propellants can be observed by flowing water through the tubes and illuminating the stream with a strobe light. If liquid nitrogen is substituted for the water and the impinging streams are again illuminated, the behavior of a boiling liquid can be observed. These observations can also be made with an actual combustor if it is equipped with special windows. Such a combustor has been used at Lewis Research Center for studies of alcohol burning in vaporized oxygen, oxygen streams burning in vaporized oxygen, oxygen streams burning in hydrogen, and impinging streams of hypergolic propellants, all at a combustion-chamber pressure of approximately 20 atmospheres. Photographs obtained in these studies are presented in figure 4-7. The results of such tests are used to determine what mathematical model is to be used to describe the behavior of a particular propellant combination.

Combustion follows very rapidly after mixing has taken place. The gaseous products increase in velocity toward the nozzle and mix with the unburned propellants as they go. Ideally all the unburned propellants mix, react, and mix again as products before they reach the nozzle. Incomplete mixing and incomplete reaction result in reduced rocket efficiency, which in turn, reduces the payload.

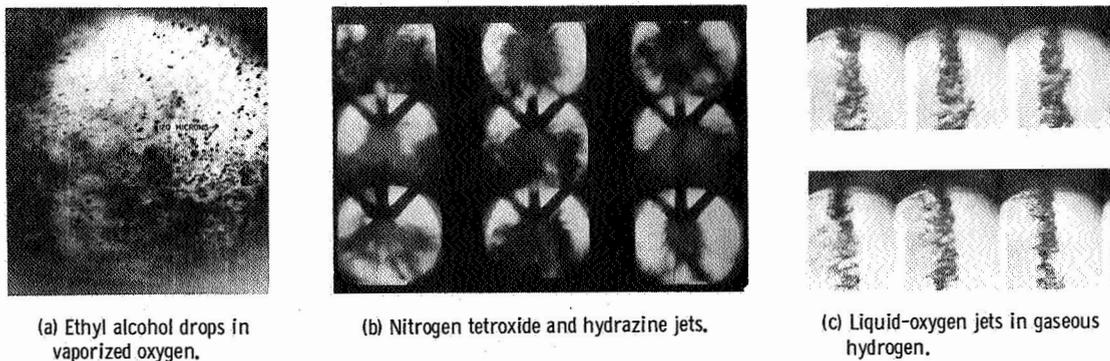
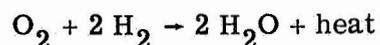
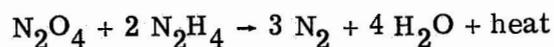
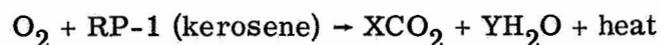
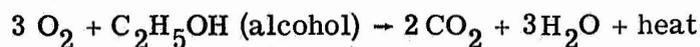
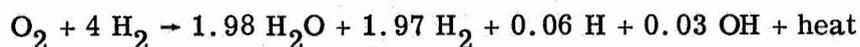


Figure 4-7. - Liquid-propellant vaporization and combustion. Combustion-chamber pressure, 20 atmospheres.

The simplest way to state the combustion reaction of a liquid propellant combination is to write the equation that describes it. The following equations describe the combustion reactions of the liquid propellants which have been discussed previously:



The actual reaction for each of these propellant combinations is not as simple as shown in these equations. One reason for this is that there are more products than shown here. Another reason is that the oxidant-fuel weight ratio O/F for highest impulse is fuel rich (that is, there is not enough oxidant to react with all the fuel). Hence, the actual reaction of oxygen and hydrogen can be described more accurately by the following equation:



The combustion of composite solid propellants (fig. 4-8) is somewhat analogous to that of liquid-propellant mixtures. Solid-propellant surface heating takes the place of the injection process. Solid or liquid fuel and oxidizer particles decompose to form gases which subsequently react. Since the solid propellant is an excellent insulator, the solid is heated at or very near the surface until the oxidizer and fuel start decomposing at their common boundaries. Soon the oxidizer particles are no longer held in place by the fuel

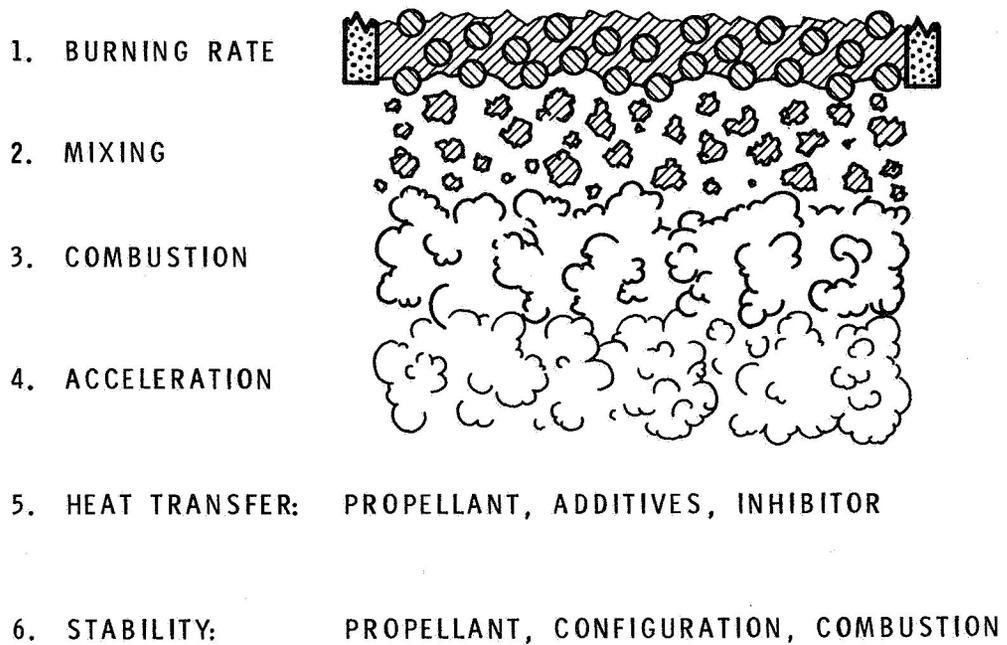


Figure 4-8. - Composite-propellant combustion.

binder, and they break loose to be carried along in the gas stream with the decomposing binder. Other materials such as metallic particles of aluminum are sometimes added to the composite propellant for better combustion and higher impulse. Also, the burning aluminum is a great aid in the observation of the burning of the propellant (fig. 4-9).

The reaction of a double-base propellant is different from that of a composite because the oxidizer and fuel of the double-base propellant are chemically mixed rather than just in physical proximity to each other. In order to describe the burning of a double-base propellant it is necessary to consider three zones called the foam, fizz, and flame zones. Heating very close to the surface melts some of the propellant and causes some low-

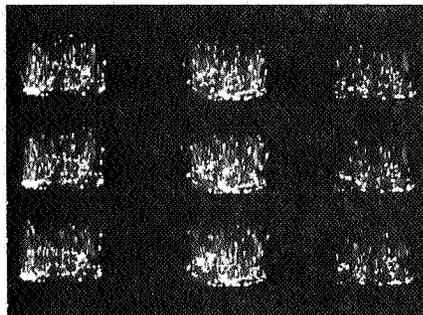


Figure 4-9. - Burning composite propellant with added aluminum. Pressure, 1 atmosphere.

temperature reactions. Bubbles of gas are released (foam zone) which rise and enter the fizz zone, where the remaining propellant decomposes. Final reactions and flame temperature occur in the flame zone.

Thus far the discussion has centered on the characteristics and the behavior of the propellants. The following discussion pertains to the combustion chamber. At the end of the chamber opposite the nozzle, there is an injector in the liquid-propellant engine, and there is usually a layer of solid propellant and inhibitor in the solid-propellant engine. In the liquid-propellant engine there is sufficient liquid entering the combustion chamber from the propellant manifold to prevent melting or burning of the injector face. However, care must be taken to prevent very hot, oxidizer gases from hitting the surface of the chamber wall at high velocity, because these gases can act just like a cutting torch. In the solid-propellant engine, a layer of propellant and inhibitor prevents overheating of the combustion-chamber walls, so the walls need only be strong enough to withstand the chamber pressure. As the solid propellant is burned away, the inhibitor acts as a heat shield and as a very slow burning fuel (fig. 4-10). Latex paint is a good example of an inhibitor.

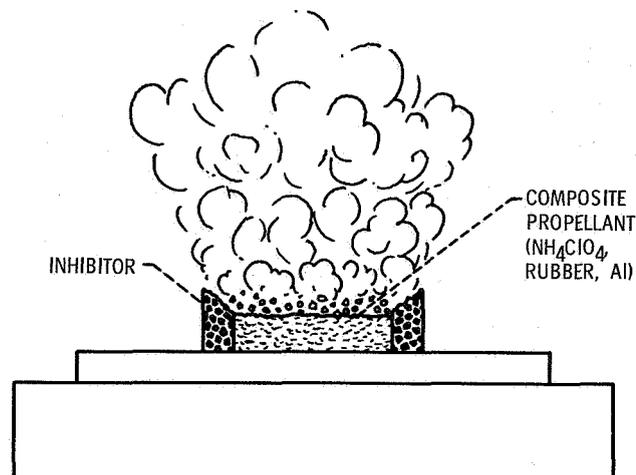


Figure 4-10. - Burning strand of solid propellant.

The combustion-chamber walls of a liquid-propellant engine are more complex than those of a solid-propellant engine. One of the liquid propellants, usually the fuel, passes at high velocities through thin tubes on its way to the injector. The tubes form part of the outside chamber walls. This procedure is called regenerative cooling and helps to prevent overheating of the chamber walls. Sometimes regenerative cooling is not sufficient to ensure cool walls. Then part of the liquid fuel is sprayed on the inner surfaces of the walls to act as a liquid or vapor shield against the heat from the combustion

gases. This procedure is known as film cooling. Of course, the walls must be strong enough to contain the chamber pressure.

The nozzle of a liquid-propellant engine is cooled the same way as the chamber walls (regenerative and film cooling). But the nozzle of a solid-propellant engine is necessarily uncooled. Therefore, it is made of a strong heat-resistant material such as tungsten, graphite, or a metal-ceramic combination.

Normally, there are low-velocity, cool gases close to the inside surfaces of the chamber walls. These cool gases help to shield the walls from the high-velocity, hot gases in the center of the chamber. If the cool gases are removed, the wall surfaces may burn out in the liquid-propellant engine, or they may erode in the solid-propellant engine. Pressure oscillations within the chamber can have the same effects, and they can even rupture the chamber walls themselves. These pressure oscillations are known as combustion instability. One form of combustion instability is called chugging and is characterized by severe oscillations in pressure at low frequencies (<100 cps). Another form of combustion instability is characterized by severe, high-frequency oscillations in pressure and is called screaming.

Chugging can be compared to a surging in which the propellants flow alternately at low and high velocities. The chamber pressure then responds to this flow behavior. Chugging may not be destructive to the engine itself, but it can result in violent shaking of the whole rocket structure.

Screaming can be compared to the pressure vibrations in pipe-organ tubes. Pressure waves can travel at sonic velocities up and down the chamber length, around it, across it, or radially in and out (fig. 4-11). All these high-frequency oscillations have been measured in research engines. Waves around the chamber have recently been produced in a specially built engine which can burn liquid propellants ( $O_2$  and  $H_2$ ) or solid composite propellants. Figure 4-12 shows stable and unstable combustion with both types of propellant.

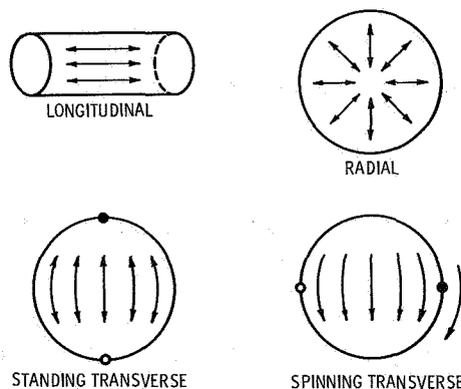
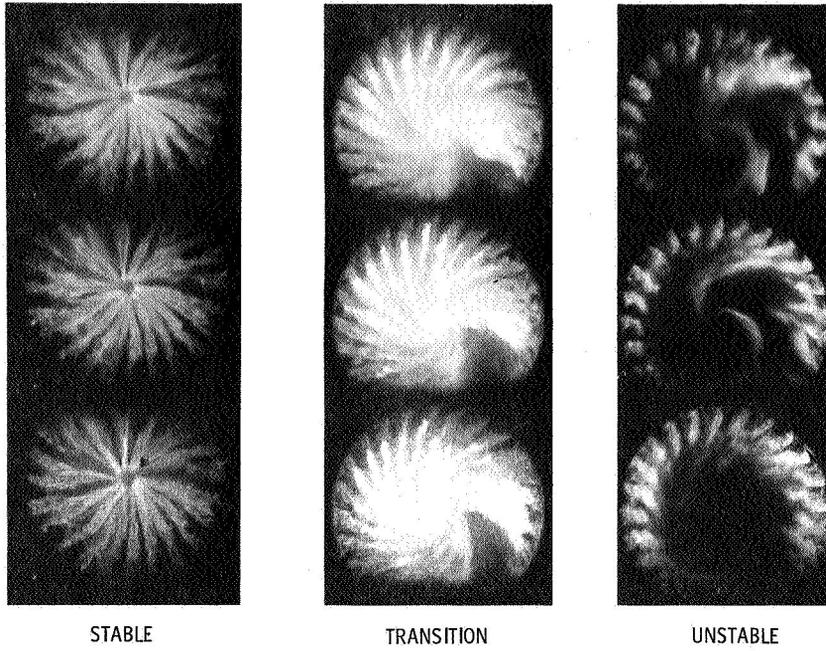
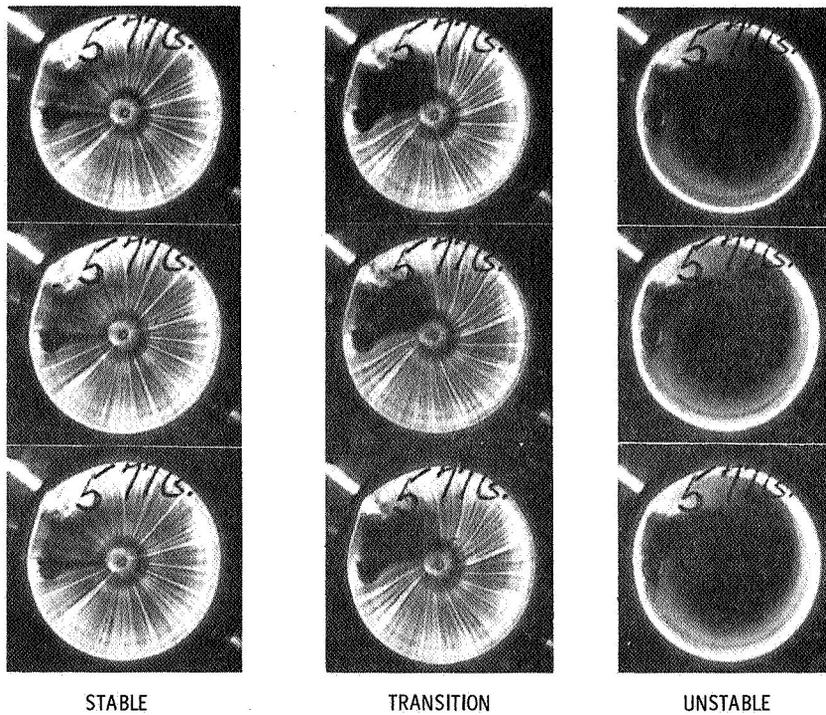


Figure 4-11. - Fundamental modes of acoustic combustion instability.



(a) Combustion of liquid-oxygen - liquid-hydrogen propellant.



(b) Combustion of composite propellant.

Figure 4-12. - Screaming in liquid- and solid-rocket combustors.

In this chapter, a general discussion of the development, uses, burning processes, and problems of propellants has been presented. However, no attempt has been made to select the "best" propellant, injection method, or combustion-chamber shape. There really is no absolute best in these things, because no one propellant has all the desirable characteristics, and because the combustion-system hardware must be optimized for each propellant combination. The principal desirable features of propellants and of combustion systems are presented in the following lists.

Propellants:

- (1) High chemical energy (high impulse, high temperature)
- (2) Low molecular weight of combustion products
- (3) Chemical stability during storage
- (4) Small variation of physical properties with temperature
- (5) No change in state at storage temperature
- (6) High propellant density
- (7) Predictable physical and combustion characteristics
- (8) Easily ignitable, but safe and nontoxic during storage
- (9) Stable, efficient burning behavior
- (10) Nonluminous, smokeless, nontoxic exhaust

Combustion systems:

- (1) Injector or grain optimized for most stable, efficient combustion
- (2) Use of minimum chamber volume necessary for maximum system efficiency
- (3) Nozzle shape optimized for propellants and mission

## GLOSSARY

ablation. Removal of surface material from a body by sublimation, vaporization, or melting due to heating resulting from a fluid moving past it at high speed. This phenomenon is often used to protect a structure from overheating by providing an expendable ablation surface, such as the heat shield on a reentry vehicle, or a protective coating in a combustion chamber.

additive. A substance added to a base to achieve some purpose such as a more even rate of combustion in a propellant or improved lubrication properties of working fluids such as RP-1, etc.

airbreathing engine. An engine which requires the intake of air for combustion of the fuel, as a ramjet or turbojet. This is contrasted with the rocket engine, which carries its own oxidizer and can operate beyond the atmosphere.

alcohol. See ethyl alcohol.

ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ). Solid compound used as an oxidizer in composite propellants. Available oxygen content is low, so high percentages are required for high performance. Exhaust contains very little smoke.

chemical fuel. A fuel depending on an oxidizer for combustion or for development of thrust, such as liquid- or solid-rocket fuel, jet fuel, or internal-combustion engine fuel; distinguished from nuclear fuel.

chemical rocket. A rocket using chemical fuel.

chugging. A form of combustion instability in a rocket engine, characterized by a pulsing operation at a fairly low frequency, sometimes defined as occurring between particular frequency limits.

combustion. A chemical process characterized by the evolution of heat; commonly, the chemical reaction of fuel and oxidizer; but, by extension, the term includes the decomposition of monopropellants and the burning of solid propellants.

combustion instability. Unfavorable, unsteady, or abnormal combustion of fuel, especially in a rocket engine. Unfavorable combustion oscillation such as chugging or screaming.

combustion chamber. See thrust chamber.

composite propellant. A solid rocket propellant consisting of an elastomeric fuel binder, a finely ground oxidizer, and various additives.

cryogenic propellant. A rocket fuel, oxidizer, or propulsion fluid which is liquid only at very low temperatures.

ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH). Colorless liquid used extensively in the chemical and liquor industries. Used with water as the fuel in the German V-2 rocket. (25 percent H<sub>2</sub>O, 75 percent C<sub>2</sub>H<sub>5</sub>OH).

film cooling. The cooling of a body or surface, such as the inner surface of a rocket combustion chamber, by maintaining a thin fluid layer over the affected area.

hybrid motor. A rocket-propulsion unit that burns a combination of propellants of different composition and characteristics (as a liquid oxidizer and a solid fuel) to produce a propulsive force.

hydrazine (N<sub>2</sub>H<sub>4</sub>). Toxic, colorless liquid with high freezing point (34° F); soluble in water and alcohol; very flammable and burns by itself (monopropellant).

hydrogen. Lightest chemical element; flammable, colorless, tasteless, odorless gas in its uncombined state; used in liquid state as a rocket fuel; boiling point of -423° F.

hydrogen-fluorine. High-energy liquid propellant for rocket engines. Hydrogen is the fuel and fluorine is the oxidizer.

hypergolic fuel. Rocket fuel, such as hydrazine, that ignites spontaneously upon contact with the oxidizer and thereby eliminates the need for an ignition system.

inhibitor. A substance bonded, taped, or dip-dried onto a solid propellant to restrict the burning surface and to give direction to the burning.

initiator. A unit which receives electrical or detonation energy and produces a chemical deflagration reaction.

liquid hydrogen. Supercooled hydrogen gas, usually used as a rocket fuel; boiling point is -423° F; low density requires bulky, well insulated tanks and lines; very flammable.

liquid oxygen (LOX). Supercooled oxygen used as the oxidizer in many liquid-fuel engines; boiling point is -297° F; burns with fuels, metals, and organic materials.

liquid propellant. A liquid ingredient used in the combustion chamber of a rocket engine.

multipropellant. A rocket propellant consisting of two or more substances fed separately to the combustion chamber.

nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>). Yellow-red, toxic oxidizer used in storable-liquid-propellant systems. Reacts spontaneously with fuel and many other materials; very corrosive; boiling point is 70° F; stable at room temperature.

nozzle. The part of a rocket thrust-chamber assembly in which the gases produced in the chamber are accelerated to high velocities.

oxidizer. A substance that supports the combustion reaction of a fuel.

oxygen. See liquid oxygen.

oxygen-hydrocarbon engine. A rocket engine that operates on propellant of liquid oxygen as oxidizer and a hydrocarbon fuel such as a petroleum derivative.

propellant. A liquid or solid substance or substances which either separately or mixed can be changed into a large volume of hot gases at a rate which is suitable for propelling projectiles or air vehicles.

rocket engine. A reaction engine that contains all the substances necessary for its operation or for the consumption or combustion of its fuel. Does not require intake of any outside substance, and is capable of operation in outer space. Also called rocket motor.

rocket propulsion. A type of reaction propulsion in which the propulsive force is generated by accelerating and discharging matter contained in the vehicle. To be distinguished particularly from jet propulsion.

RP-1. Rocket propellant, type 1, is a nearly colorless liquid fuel resembling kerosene in its characteristics; contains a variety of hydrocarbon chemicals; boils at temperatures from 220<sup>o</sup> to 570<sup>o</sup> F; easily storable at normal temperatures.

screaming. A form of combustion instability, especially in a liquid-propellant rocket engine, of relatively high frequency and characterized by a high-pitched noise.

solid propellant. Specifically, a rocket propellant in solid form, usually containing both fuel and oxidizer combined or mixed and formed into a monolithic (not powdered or granulated) grain.

stoichiometric. Of a combustible mixture, having the exact proportions required for complete combustion.

subsonic. Of or pertaining to speeds less than the speed of sound.

supersonic. Of or pertaining to speeds greater than the speed of sound.

thermodynamics. The study of the relations between heat and mechanical energy.

thrust. The pushing force developed by an aircraft engine or a rocket engine. Specifically, the product of propellant mass flow rate and exhaust velocity relative to the vehicle.

thrust chamber. The chamber of a jet or rocket motor in which volume is increased through the combustion process to obtain high velocity gases through the nozzle.

UDMH. Unsymmetrical dimethyl hydrazine, a clear, colorless liquid with low freezing point, -71<sup>o</sup> F; boils at +146<sup>o</sup> F; soluble in water, ethyl alcohol, and most hydrocarbon fuels; one of a group of fuels known as the amines; mixed equally with hydrazine to form Aerozine; used in numerous current engines.

vaporization rate. The unit mass of a solid or liquid that is changed to a vapor or gas in a unit of time.

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